(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁷: C04B

(21) International Application Number: PCT/US02/08913

(22) International Filing Date: 22 March 2002 (22.03.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/278,015   22 March 2001 (22.03.2001)   US
Not furnished   21 March 2002 (21.03.2002)   US

(71) Applicant: CLEMSON UNIVERSITY [US/US]; 300 Brackett Hall, Clemson, SC 29634-5701 (US).

(72) Inventors: CARROLL, David; 219 Luna Lane, Central, SC 29630 (US). BALLATO, John; 811 Issaqueena Trail, Central, SC 29630 (US). FOULGER, Stephen; 301 Monaco Circle, Clemson, SC 29631 (US). CZERW, ..

Richard; 102 Sedgefield Drive, Clemson, SC 29631 (US). SMITH, Dennis; 3010 North Bayshore Drive, Seneca, SC 29672 (US). SHAH, Hiren; 146 Folger Street, Clemson, SC 29631 (US). WAGENER, Earl; 216 Strawberry Lane, Clemson, SC 29631 (US).

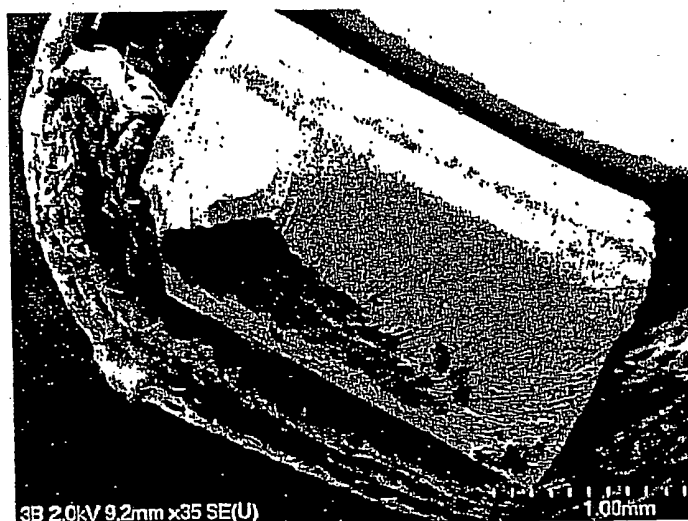(74) Agent: DORITY & MANNING, P.A.; P.O. Box 1449, Greenville, SC 29602 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,

(54) Title: HALO-POLYMER NANOCOMPOSITE COMPOSITIONS, METHODS, AND PRODUCTS EMPLOYING SUCH COMPOSITIONS

3B 2.0kV 9.2mm x35 SE(U)   1.00mm

(57) Abstract: The disclosure provides compositions prepared by combining nanomaterials with a halide-containing polymer, thereby forming a combined polymer matrix having dispersed nanomaterials within the matrix. The nanomaterials may be carbon-based nanotubes, in some applications. A halide-containing monomer is combined with nanotubes, and then polymerized in some compositions. In other applications, a holide-containing polymer is solution processed with nanotubes to form usefuld compositions in the invention. Also disclosed are probes for near field detection of radiation.

GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Title of the Invention

HALOGEN CONTAINING-POLYMER NANOCOMPOSITE
COMPOSITIONS, METHODS, AND PRODUCTS EMPLOYING
SUCH COMPOSITIONS

Cross-Reference to Related Applications

5   This application claims priority to an earlier filed provisional
application, S. N. 60/278,015, filed in the United States on March 22,
2001; and also upon a regular U.S. utility patent application Serial No.
Not yet known filed 21 March, 2002 entitled "HALOGEN

10   CONTAINING-POLYMER NANOCOMPOSITE COMPOSITIONS,
METHODS, AND PRODUCTS EMPLOYING SUCH
COMPOSITIONS".

Field of the Invention

The invention is directed to uniquely homogeneous dispersions

15   of nanometer-sized materials in halogen-containing polymers.

Background of the Invention

To materials engineers, composites offer the ability to alter the
properties of materials by combining the functionalities of several
components for a specific purpose. It is widely believed that, for

20   example, ceramic/polymer nano-engineered composites can be
designed to exhibit the overriding strength, dimensional, and thermal
stability of ceramics with the fracture properties, processability, and
dielectric properties of polymers. "Matrix Nanocomposites" are a new
class of materials, which exhibit ultra-fine dispersed phase

25   dimensions, typically in the 1-100nm range as well as a physically
distinct host or continuous phase over much longer average length
scales. The nano-length scale is the range where phenomena
associated with atomic and molecular interactions strongly influence
the macroscopic properties of materials such as electrical and thermal

30   conductivity, strength, and optical clarity, for example, the longer
length scale phase are typically used – in addition to the afore
mentioned macroscopic properties -- to determine processing and
fabrication of the composite.

Preliminary experimental work on nano-composite materials have suggested that many types and classes of nanocomposites have new and improved properties when compared with their macro-scale counterparts (see for example: Ajayan, P.M. *Chem. Rev.* 1999, *99*, 1787). A predominant feature of these materials is their ultra fine phase dimension and hence surface area; therefore a large fraction of the atoms reside at an interface. The properties can therefore be expected to be strongly influenced by the nature of the interface. For example, a strong interface should allow unusual mechanical properties. Since the interface structure plays a critical role in determining the properties of these materials they are frequently referred to as "interface composites".

To make a successful nanocomposite it is very important to be able to disperse the secondary phase (be it a nanosized metal, ceramic, or polymer) throughout the host material and create those interfaces.

Nanocomposites are now becoming viable commercial products. BIB.: Y. Feng, Y. Ou, Y. Zhongzhen, *J. Appl. Polym. Sci.*, 69(2), 355, 1998.). Most research and development is focused on automotive parts and packaging, and space durable composites ("Fluoropolymer Nanotube Composites for Coatings and Nanoscopic Probes" Shah, H.; Czerw, R.; Carroll, D.; Goldner, L.; Hwang, J.; Ballato, J.; Smith, Jr., D.W. *Polym. Mat. Sci. & Eng. (Am. Chem. Soc., Div. PMSE)* 2000, *82*, 300.), display applications (P.M.Ajayan, O. Stephan, C. Colliex, and D. Trauth, *Science*, 265, 1212, 1994.), and atomic force microscopy (AFM) probes (Dai, H.; Hafner, J.H.; Rinzler, A.G.; Colbert, D.T.; Smalley R. E. *Nature*, 1996, *384*, 147 and Hafner, H.G.; Cheung, C.; Lieber, C.M. *Nature*, 1999, *398*, 761).

The benefits of such nanocomposites that have already been identified include: efficient reinforcement with minimal loss of ductility, improved impact strength, heat stability and flame resistance, improved gas barrier properties, improved abrasion resistance, reduced shrinkage and residual stress, altered electronic and optical properties (See for example: "Handbook of Nanophase Materials" A.

N. Goldstein, Ed., Marcel Dekker, Inc., New York, 1997 and S.J
Komarnemi, *Mater. Chem.*, 2, 1219, 1992). The shapes of the
particles used in nanocomposites can vary from spherical, fibrilar, to
platelets, and each will result in different properties modifications to
the host. For example: for maximum reinforcement, platelets or
fibrilar particles would be used, since reinforcement efficiency tends to
scale with the aspect ratio (L/d). Further, performance benefits of
nanoparticulate fillers are available without increasing the density or
reducing light transmission properties of the base polymer. Although
many research projects have been reported concerning all types of
nanoparticles, the most extensive research has been performed with
layered silicates, which provides platelet reinforcement.

Matrix nanocomposites, based on polymers, have been a
central area of polymer research in recent years and significant
progress has been made in the formation of various types of polymer-
nanocomposites. This includes an understanding of the basic
principles that determine their optical, electronic and magnetic
properties. An early polymer nanocomposite that was developed was
the polyamide 6 (from caprolactam), which has dispersed ion-
exchanged montmorillonite, a smectic clay, as the reinforcement.
Such nanocomposites typically contain 2-10% loadings on a weight
basis, yet property improvements can equal and sometimes exceed
traditional polymer composites even containing 20-35% mineral or
glass. Machine wear is reduced and processability is better. Because
polymers are, typically, about one-half as density as mineral and glass
fillers these composites offer attractive opportunities for weight
sensitive applications, such as auto parts.

Fluoropolymers are known to represent viable alternatives to
current optical materials particularly for the critical next step in optical
communications – access level all-optical networks (*Modern
Fluoropolymers*, Scheirs, J., Ed.; Wiley: New York, 1997).

A pending United States Patent application, U.S. Serial Number 09/604,748 entitled "Fluoropolymers and Methods of Applying Fluoropolymers in Molding Processes" and assigned to the assignee of the present application is directed to uses of PFCB compounds in molding processes and optical applications.

Other publications have recited various synthesis methods and uses for PFCB and fluoropolymeric compounds. See, i.e. Smith et al, "Perfluorocyclobutyl Liquid Crystalline Fluoropolymers. Synthesis and Thermal Cyclopolymerization of Bis(trifluorovinyloxy)-alpha-methylstilbene", *Macromolecules*, Volume 33, Number 4, Pages 1126-1128; See also Smith et. al. "Perfluorocyclobutane (PFCB) polyaryl ethers: versatile coatings materials", Journal of Fluorine Chemistry 4310 (2000) 1-9. There is great potential for this optical fluoropolymer to further enhance its properties by using it in a nanocomposite where the nanomaterial provides unique interactions with light.

In regards to electrically conductive polymer composites, work has been done using carbon black as a second phase to permit conductivity in an otherwise dielectric host. See Foulger, Stephen: *"Reduced Percolation Thresholds of Immiscible Conductive Blends"*, Journal of Polymer Science: Part B: Polymer Physics, Vol. 37, 1899-1910 (1999).

Although carbon black was used in the previous case, many forms of carbon exist. For example carbon may be in the form of submicron graphitic fibrils, sometimes called "vapor grown" carbon fibers. Carbon fibrils are vermicular carbon deposits having diameters less than about 1.0 micrometer. They exist in a variety of forms and have been prepared by catalytic decomposition of carbon-containing gases on metal surfaces.

United States Patent No. 4,663,230 discloses cylindrical ordered graphite cores, uncontaminated with pyrolytic carbon. Blending such fibers with polymers has been known to improve the mechanical properties of the resulting blends.

More recently, it has been found that carbon tubes (often termed "nanotubes") provide a structure with potential for many such applications. In particular, the structure of carbon nanotubes makes their aspect ratio (length/diameter, L/D) comparable to that of long fibers. Typically the aspect ratio of carbon nanotubes is >10,000. Thus, the aspect ratio of carbon nanotubes is generally much greater than that of conventional short fibers, such as those often made of glass or other forms of carbon. In addition, nanotubes sometimes may be lighter than conventional carbon fibers, which may be helpful in some applications.

Currently, carbon nanofibers and carbon nanotubes figure prominently among the organic-host nanocomposite fillers of interest. Vapor grown carbon nanofibers (VGCFs) in thermoplastic matrices have attracted much interest as they have potential application as conducting polymers for electrostatic dissipative coatings. In addition the VGCFs enhance both stiffness and thermal stability of the matrix. Thermoplastic matrices noted in recent studies include polypropylene, acrylate-butadiene-styrene, polyethylene, polycarbonate and polyether-terephthalate. Naturally, the interactions between the fiber and the matrix at the interfacal level are of critical importance to the properties of the developed composite. The catalytically grown carbon fibers used in these previous studies have outstanding physical properties such as high tensile modulus as well as low electrical resistivity and high thermal conductivity (1,950W/mK). Further, these nanofibers can be surface-treated to promote different types of bonding. However, electrical and thermal conductivities as well as yield strengths and moduli are orders of magnitude larger for carbon nanotubes and one might want to extend these nanocomposites to include nanotube dispersions instead of VGCFs. This is because network formation at the percolation threshold of nanotubes may be achieved at relatively low mass concentrations because of their unusually high aspect-ratios. Hence, enhanced electrical and thermal conductivity may be possible in

polymer/nanotube composites without sacrificing, for example, host optical clarity or flexibility.

Unfortunately, control over dispersive characteristics is significantly more difficult for carbon nanotubes. This comes about because, unlike VGCF, the surfaces of the nanotubes are exceedingly difficult to modify as they exhibit, primarily, unreactive carbon-carbon bonds.

Efforts have been made to incorporate carbon nanotubes into hydrocarbon-based polymeric materials, but difficulty has been encountered in providing compositions that perform well. In general, the number of carbon nanotubes that must be placed into a polymeric composition to achieve superior properties is so high that the actual physical and structural properties of the polymer may be deteriorated by the presence of the carbon nanotubes. This difficulty may be due to the fact that carbon nanotubes tend to clump and aggregate together (instead of uniformly dispersing) when placed in many hydrocarbon-based polymeric compositions.

This relatively poor control over the dispersive characteristics has made it difficult to employ carbon nanotubes in useful applications. The surfaces of such nanotubes may be exceedingly difficult to modify as well, since nanotubes exhibit primarily unreactive carbon-carbon bonds.

What is needed in the industry is a composition and method of preparing a composition that is capable of employing the useful properties of nanomaterial structures in a polymer matrix. A composition that successfully combines nanomaterial structures uniformly dispersed in a polymer matrix would be highly desirable.

Summary of the Invention

The invention is directed to uniquely homogeneous dispersions of nanometer sized materials in halogen-containing polymers. Such compositions may include the use of nanotubes such as carbon-based nanotubes. Furthermore, nanotubes may be mixed into a halogen-containing polymer matrix. A halogen-containing monomer and/or polymer forms a compositional matrix with nanotubes. In

some applications, a halogen-containing polymer is combined with nanotubes to achieve a relatively high level of nanotube dispersion. The homogeneity of the dispersion are superior in the invention.

5   Some specific applications of the invention employ fluoropolymers, while other specific applications may employ chloropolymers as the host polymer. Various products may employ compositions made according to the invention. These products and applications include: light emitting devices, nanoscopic probes, thermal management, electrical conductivity, electromagnetic

10   interference, EMI shielding, linear and nonlinear optics (for example optical limiting), polymer actuation, and stealth (where each material can be in film, fiber, powder, liquid resin, or solution form), and others as well. This list is not exhaustive, and certainly other applications for the compositions exist as well, such as, for example, "dual function"

15   applications involving multiples of the above properties. In particular, polymer electrical conductivity in addition to optical clarity represents a major need in applications requiring light transmission and static charge dissipation (e.g., for space durable optical film).

      A number of factors combine to fuel interest in polymer based

20   nanocomposite technology using clay minerals which include low loading levels, transparency, incorporation flexibility, safety, synergies with other additives and low cost. In the past, combinations of clays in such materials have not been compatible with polymers and hence surface modified to render them hydrophobic. Polymers such as

25   polyimide, epoxy resin, polystyrene, polycaprolactone, acrylic polymer and polypropylene have been explored to fabricate polymer nanocomposites using clays which form the main inorganic nanocomposites.

<u>**Brief Description of the Drawing**</u>

30   The following Figures illustrate the invention:

      Figures 1a-c show photographs of a PFCB composite;

      Figures 1d-f show photographs of PVDF, as further discussed herein;

Figures 2a-c include photos of samples of composites of PVDF/HFP, as further discussed herein;

Figure 3 compares the absorption curves from the PFCB materials with those of PVDF and PVDF-copolymer nanocomposites;

Figure 4 shows scattered light at 500 nm from PFCB, PVDF, and PVDF-copolymer;

Figure 5 is a 1 mm thick film of polymethylmethacrylate (PMMA);

Figure 6 is a Table showing surface energies and fluorine content for the polymers featured in the study herein;

Figure 7 is a graph of wavelength versus absorption, as further discussed herein;

Figure 8a shows a drawn PFCB fiber containing carbon nanotubes; and

Figure 8b illustrates a probe having a nanocomposite fiber with a nanotube protruding from the frontal surface of the probe.

Detailed Description of the Invention

Reference now will be made to the embodiments of the invention, one or more examples of which are set forth below. Each example is provided by way of explanation of the invention, not as a limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in this invention without departing from the scope or spirit of the invention.

Both organic and inorganic nanomaterials may be combined with halogen-containing monomers or halogen-containing polymers in the practice of the invention. Among the inorganic nanomaterials, some may be based on clays, such as montmorillonite, kaonite, bentonite, mica, talc, silica nanoparticles and the like as further disclosed in Examples below.

"Nanocomposite materials" or "nanocomposites" as used herein shall include a class of materials that exhibit ultra-fine phase dimensions, typically in the 1-100 nm range, as well as a physically distinct host phase existing over much longer average length scales. The nano-length scale is the range in which phenomena associated

with atomic and molecular interactions strongly influence the macroscopic properties of materials such as electrical and thermal conductivity. Longer length scales may be used to determine processing parameters of the materials. Although the following discussion focuses primarily on polymer/carbon nanotube-based nanocomposites, in general, "nanocomposite materials" and "nanocomposites" as used herein also refers to other nanosized materials such as, but not limited to, those comprised of Group III-through-Group V-elements, transition metal oxides (e.g., vanadium oxide), and others.

Further, in regards to inorganic/polymer nanocomposites there are at least two types of inorganic layered silicate/polymer nanocomposites, i.e. intercalates and exfoliates, depending upon the organization of the silicate layers. Intercalates are obtained when polymer is located between the silicate layers and while the layer spacing is increased. There are attractive forces between the silicate layers which cause the layers to be provided in regularly spaced stacks. Exfoliates are obtained when the layer spacing increases to the point at which there no longer is sufficient attraction between the silicate layers to cause a uniform layer spacing. In exfoliates, silicate layers are randomly dispersed throughout the composite.

Organosilicates may be more compatible with engineering plastics, as they usually contain various functional groups that interact and/or react with the polymer to improve adhesion between the inorganic phase and the matrix.

Various methods of synthesis may be employed:

(1) Nanomaterials can be solution mixed with dissolved pre-formed polymer.

(2) Nanomaterials can be melt mixed with molten pre-formed polymer.

(3) Nanomaterials can be solution mixed with *insitu* solution polymerization of the host polymer.

(4) Nanomaterials can be melt mixed with *insitu* melt polymerization of host polymer.

(5) Nanomaterials can be mixed via multi-phase processes involving both pre-formed polymer and/or *insitu* polymerization such as, aqueous dispersion or emulsion polymerization with or without the addition of surfactants.

(6) Nanomaterials can be mixed with pre-formed polymers or by *insitu* polymerization as described in 1-5 above with or without the aid of heat and sonication.

(7) Nanomaterials can be mixed with sol-gel precursors such as tetraalkoxysilanes (eg., TEOS or TMOS) or otherwise organic functional trialkoxysilanes and polymerized by catalytic hydrolysis to a silicate or silicate / organic hybrid nanocomposite.

Carbon nanotubes are one type of nanomaterial (single-walled or multi-walled) that sometimes behave like one dimensional metallic conductors or low band gap semi-conductors. Incorporation of carbon nanotubes in insulating polymer matrices may increase the electrical conductivity of the composites by several orders of magnitude. For purposes of this specification the term "nanotube" shall refer to a nanomaterial that assumes a tubular or cylindrical shape.

Carbon nanotubes may act as nanometric heat sinks. Network formation or percolation threshold of nanotubes may be achieved at relatively low concentrations because of their unusually high aspect ratios. Hence, enhanced electrical and thermal conductivity may be obtained in polymer/nanotube composites, without sacrificing optical clarity, since their diameter is sufficiently small that light is not strongly absorbed or scattered.

It is advantageous in many industries (including electronics, optoelectronics, and aerospace) to have mechanically flexible electrically and thermally conductive coatings and substrates. In addition, composites possessing these features and optical clarity are desired. In the present invention, the halopolymer nanocomposites possess the requisite thermal and electrical conductivities. More specifically, for aerospace structures, a conductivity of ca. 10^{-7} S/cm is needed for static charge dissipation. Further, management of

thermal cycles on aerospace structures also is desired. The halopolymer nanocomposites exhibit adequate thermal and electrical conductivity for these applications while maintaining mechanical flexibility and toughness as well as optical clarity. This is realized through the unique level of dispersion for very low loadings (<0.1 to 5 weight %) of high conductivity nanotubes afforded by the halopolymer host comprised in the nanocomposites disclosed in the invention.

It has been found that halogen-containing polymers exhibit unique compatibility with carbon nanotubes, and that such nanotubes may be dispersed by simple solution or melt processes to provide unique levels of homogeneity. In this invention, the dispersion properties of carbon nanotubes are disclosed for several halogen-containing polymer matrix formations.

In making the compositions of the invention, it is possible to combine nanotubes with halogen-containing monomers. It also is possible to combine nanotubes with halogen-containing polymers. That is, polymerization may occur either before or after application of nanotubes, depending upon the particular application. Copolymers also may be used.

The invention is comprised, in one embodiment, of a composition prepared by combining nanomaterials with a halogen-containing polymer or monomer to form a nanocomposite. In one application of the invention, carbon nanotubes may be dispersed in a halogen-containing polymer by melt or solution processing to form a nanocomposite. Furthermore, at low nanotube loading levels, the resulting composition may be formed into a transparent film, fiber, powder, liquid resin, or solution.

A "halogen-containing polymer" or "halogen-containing monomer" as described herein and as employed in the invention may include essentially any or all Group VII elements within a polymeric structure. The halogen species may be fluorine, chlorine, bromine or iodine, for example, depending upon the particular application.

In one specific aspect of the invention, the halogen-containing polymer comprises a fluoropolymer such as those derived from

monomers containing trifluorovinyl ether (TFVE) groups (as initially
described in: "Fluoropolymer Nanotube Composites for Coatings and
Nanoscopic Probes" Shah, H.; Czerw, R.; Carroll, D.; Goldner, L.;
Hwang, J.; Ballato, J.; Smith, Jr., D.W. *Polym. Mat. Sci. & Eng. (Am.*
Chem. Soc., Div. PMSE) 2000, *82*, 300).

Whereas these polymers are receiving consideration for
structural composites, there are commercial applications of equal
importance for optical composites. From a potential host materials
perspective, perfluorocyclobutane (PFCB) polymers have suggested
for use in optical fibers and dielectric waveguides. See, for example,
"Property Tunable Perfluorocyclobutyl (PFCB) Copolymers for Optical
Devices" Smith, Jr., D.W.; Kumar, S.; Chen, S.; Ballato, J.; Nelson, E.;
Jin, J.; Foulger, S. in *Design, Manufacturing, and Testing of Planar*
Optical Waveguide Devices, R.A. Norwood, Ed. *SPIE Proc.* 2001,
4439, 51-62.

In specific applications, the fluoropolymer may comprise a
perfluorocyclobutane (PFCB) aromatic ether moiety, as further
discussed herein. In still other applications, other halogen-containing
polymers or monomers or copolymers may be employed, including
copolymers of PFCB, polyvinylidenedifluoride (PVDF), and
copolymers of PVDF.

Other fluoropolymers and chloropolymers that may be
employed include those polymers and copolymers made from
monomers such as: perfluoroallyl vinyl ethers, chlorotrifluoroethylene,
fluorovinyl ethers, hexafluoroisobutylene, hexafluoropropylene,
hexafluoropropylene oxide, perfluorormethyl vinyl ether, perfluoroalkyl
vinyl ether, fluoroalkylacrylates, fluoroalkylmethacrylates,
tetrafluoroethylene, vinylidene dichloride, vinyl fluoride, vinylidene
difluoride, trifluoroethylene, and vinyl chloride. Some commercial
trade names for fluoropolymers which may be employed include:
Teflon, Teflon AF, Cytop, Halar, Tefzel, Hostaflon ET, Aflon COP,
Neoflon, Teflon FEP, Hostaflon TFA, Algoflon, Neoflon AP, Kel-F,
Aclon, Voltaflef, Diaflon, Teflon PFA, Fomblin, Krytox, Denum, Teflon
PTFE, Fluon, Hostflon PTFE, polyflon, Kynar, Hylar, Solef, KF,

Tedlar, Viton A, Flurel, Technoflon, Dai-el, THV, Fluorobase T, Viton
B, Kelrez, Aflas, Kel-F 3700, Technoflon XL, Technoflon G, Viton G,
Viton GLT.

Other halogenated polymers that may be employed include:
halosilicones, halopolyurethanes, halopolyphosphazenes,
halopolycarbonates, haloepoxy resins, halopolyamides,
halopolyimides, halocyanurate resins, halopolystyrenics, halogenated
polyolefins, halopolycyclohexane, halogenated ethylene-propylene-
dienemonomer (EPDM) resins, halogenated acrylics, and
halogenated polyacrylonitriles.

Examples

The host materials used in this study are a set of four
fluoropolymers with different atomic percentages of fluorine. The
polymers, described in some detail below, are a perfluorocyclobutyl
(PFCB) aromatic polyether thermoplastic, one copolymer of PFCB,
and poly(vinylidenedifluoride) (PVDF) and one copolymer of PVDF.
These are compared to a limited extent with poly methylmethacrylate
(PMMA).

Host Materials PFCB/PFCB-Copolymer

Perfluorocyclobutyl (PFCB) polymers used were prepared from
commercially available precursors as described elsewhere.
Specifically, thermoplastic PFCB polymers used in this study were
prepared from 4,4'-bis(trifluorovinyloxy)biphenyl or
4,4'-bis(trifluorovinyloxyphenyl)hexafluoro-isopropylidene,
or for copolymers, a trifunctional comonomer
tris(trifluorovinyloxyphenyl) ethane.

Perfluorocyclobutyl (PFCB) polymers are prepared from the
free radical mediated thermal cyclopolymerization of trifunctional and
bifunctional aryl trifluorovinyl ether monomers from which a variety of
thermally stable ($T_g \sim 350°$ C), low dielectric constant thermoplastic
and thermosetting materials can be obtained. As a unique class of
partially fluorinated polymers, PFCB polyaryl ethers combine the
processability and durability of engineering thermoplastics with the
optical, electrical, thermal, and chemical resistant properties of

traditional fluoroplastics. This makes them particularly interesting for nanocomposite work.

To create the initial nanocomposite matrix, trifunctional monomer ,1,1,1-tris-(4-trifluorovinyloxyphenyl)ethane was used. Since this monomer monomer has a melting point just above room temperature (40 C), MWNTs were easily mixed with the liquid monomer by ultra-sonication for 1 hour. After sonication, the monomer/MWNT solution was a grayish, translucent liquid with very little visible aggregation. The solution was then polymerized by thermal cyclo-polymerization. The resulting nanocomposite as can be seen in figure 1b.

Host Materials PVDF/PVDF-Copolymer

The second major class of fluoropolymers used in this study, Polyvinylidene difluoride (PVDF), possesses a unique blend of properties that makes it amenable to many processing techniques and many end uses; particularly its piezoelectricity is widely utilized commercially.

PVDF is a crystalline polymer (mp. = 171°C). Since the poly(vinylidenedifluoride) for the work is commercially available , polymerization routes and synthesis chemistry will not be discussed here in detail. The copolymer of PVDF, Poly(vinylidenedifluoride-co-hexafluoropropylene) (HFP), is the other copolymer examined in this study and is generally prepared by emulsion polymerization under pressure using a persulfate-bisulphite initiation system for free radical polymerization. The PVDF itself is highly crystalline. When copolymerized with hexafluorpropylene (HFP), the degree of crystallinity is greatly reduced and its solubility in solvents is increased.

The PVDF and HFP were dissolved in N,N- dimethylacetamide (purchased from Aldrich Chemical) to give a 10% solution by weight. Occasional stirring was done to promote dissolution. To these polymer solutions weighed proportions of purified MWNTs were added and sonicated in a water bath for close to 3 hrs. The sonicated solutions look gray-black in color and are further sonicated in a probe

type sonicator (Branson Sonifier) for approximately 30 mins. The high power ultrasonication enhances the extent of mixing, which results in the presence of very little visible aggregation.

The sonicated samples were drop cast on silicon wafers heated to 120 °C. Resulting films are approximately 70-80 microns thick, with no visible aggregates. For thicker samples (~100-120 microns), films were cast in a Teflon mold. The MWNT loading used varied for different property analysis ranging from 0.1 – 35 wt%.

The molecular weights of the polymers used for these studies were approximately 50,000 for the PFCB thermoplastic and pre-network resins; and around 500,000 for the PVDFs. As noted, the PVDF tends to be rather crystalline in morphology, whereas the PFCB/ PFCB-co and PVDF-co exhibit a glassy microstructure. Volume resistivity data was collected using a Keithley 8009 Resistivity Test Fixture and Keithley Electrometer (ASTM D257).

In some applications, a composition is made having carbon-based nanotubes or nanomaterials showing a thermal conductivity greater than 1.25 W/mK at a nanomaterial loading level of about 0.01 to about 10 weight %. In other applications, the composition may show a volume resistivity of less than about 10^{10} ohm cm at a nanomaterial loading level from about 0.01 to about 10 weight %. Furthermore, in other applications a composition may exhibit an optical transmission of greater than 80% at a nanomaterial loading level of about 0.01 to about 80 weight %. In yet other applications, the composition may show an optical transmission of greater than 50% at a nanomaterial loading level from about 0.01 to about 5 weight %.

Microscopy

To first examine the microstructure of the matrix nanocomposites, we imaged fracture surfaces of the materials with a field-emission SEM (Hitachi 4700S). Shown in **figure 1** is a series images fluoropolymer nanocomposites loaded with 1% wt. of MWNTs (multiwalled carbon nanotubes). The nanophase of the composites in this study are all arc grown MWNTs with diameters ranging from 5 nm

to 30 nm and generally around 1 micron in length. **Figures 1a, b, c,** show a PFCB composite. From **figure 1a**, it is clear that settling occurs during processing. In fact, for the PFCB hosts, the nanomaterials are always observed settled to the bottom surface of

5 the films. For thinner films as used in the optical studies of this work, this effect is minimized. **Figure 1b** does show, however, that the volume of the settled material is infused with polymer and nanotubes. When the edges of the settled regions are examined **(figure 1c)** it is clear that the nanotubes are in small bundles and that agglomeration

10 has been well mitigated.

Agglomerate mitigation is also observed for the PVDF composites. Notice that while most of the nanocomposite for the 1% wt. loaded PVDF host appears extremely uniform **(figure 1d)**, occasional agglomeration of the nanophase is observed as in **figure**

15 **1e**. Naturally, it is important to realize that for the PVDF hosts used, a much higher molecular weight of the polymer is being processed than in the case of the PFCBs. This leads to higher viscosities and higher processing temperatures with the result that initial blends are not as complete. However, these large agglomerates are not extremely

20 common within the host and generally most of the nanomaterials have been effectively incorporated into the matrix.

As a demonstration of the overall clarity of the nanocomposites, **figure 1f** shows an optical micrograph of a PFCB matrix nanocomposite loaded to 0.5 % wt. This photograph is looking

25 through the 1 mm thick composite at 12 point type letters from a laser printer. The dots around the lettering are due to overspray of the printer. No aggregation of agglomeration can be seen for these large samples and the optical transmission of this particular example is approaching 80 %.

30 In **figures 2a-f**, the separation of nanotube bundles into isolated tubes is examined using both SEM and TEM (scanning electron microscopy and transition electron microscopy). In **figure 2a**, the bundles exiting the PFCB hosts indicate that tube separation is incomplete but sufficient still that the samples are optically clear (at

low tube loadings). From TEM, **figure 2b, c,** a number of isolated individual nanotubes can be seen throughout the matrix. These nanocomposites are formed without significant shear forces being added during matrix processing. Thus, nanotube separation from bundles is primarily due to wetting interactions with the host.

Optical Scattering

While electron and optical microscopy is one way of determining local dispersion characteristics, it is instructive to look at average dispersion properties over large areas. Optical scattering is a quick and easy way to understand the average particle size within the matrix. Though we will not present quantitative light scattering numbers here a comparison of the scattering for samples of the same thickness shows an interesting trend. **Figure 3** compares the absorption curves from the PFCB materials with those of the PVDF and PVDF-co nanocomposites. These films were 1 mm thick and the curves were taken using a Perkin Elmer Lambda-900 UV-Vis-NIR spectrometer. Notice in each case the strong Rayleigh component of the scattering. As is well known in optics of scattering media, this short wavelength tail is directly related to the size of the scattering particles assuming small host influences and a smoothly varying function of reflectivity and absorption. For the case of carbon nanotubes (multiwalled) these Rayleigh tails should be directly proportional to the aggregate size within the matrix. Clearly, the Rayleigh scattering has been strongly suppressed in all of the fluoropolymer composites. However, the PVDFs exhibit a stronger suppression of this scattering than does the PFCB. In fact, the PVDF-copolymer has the smallest Rayleigh scattering of any of the composites. If the light scattering at a given wavelength is compared between the different hosts, we can see that the increase in Rayleigh scattering (as a function of loading from 0.1% to 1.0%) is the strongest with the PFCBs and weaker for the PVDF-copolymer. In the example of **figure 4,** we examine the total scattered light at 500 nm from PFCB, PVDF, PVDF-copolymer. The loading in each of these hosts increases, the total scattered light from PFCB and PVDF

composites is more than double that of PVDF-copolymer composites for the same incident flux at loadings above 0.5 % wt. Since the Rayleigh component of the scatter is, by far, the largest component of this scattered light, we interpret this as meaning that the size of the aggregates within the matrices is smaller for the PVDF-copolymer composites and is larger for the PVDF and PFCB composites. Further, as expected, this aggregation grows with the loading.

Results

To understand these results in context, a comparison with optically transparent, nonfluorinated polymers is useful. Shown in **figure 5** is a 1 mm thick film of polymethylmethacrylate (PMMA). Large aggregates can be seen. These composites were created in an analogous fashion to the fluoropolymer examples discussed herein. The PMMA was solved in acetone and mixed with a suspension of MWNT, also in acetone.

Generally, microscopy and optical scattering suggests that the fluorine content of the polymers is responsible for the dispersion characteristics. In **figure 6**, surface energies and fluorine content is compared for the five polymers used in this study. The estimate of dispersion quality is, of course, subjective and based on both microscopy as well as optical scatter. The surface energies in this study were determined using a contact angle meter and Fowke's two-component model. These numbers correlate well with the suppliers for PVDF and PMMA. Notice that the surface energy is roughly the same in the case of PFCB and PMMA yet the dispersion is significantly better in the case of the fluoropolymers. Though the PFCB has a higher surface energy than that of the PVDF (PVDF-copolymer was not determined), the dispersion quality seems to scale directly with fluorine content.

Recently there have been several works discussing fluorine doping of carbon nanotubes. This suggests strong interactions between nanotubes and fluorine and suggests this as the mitigating factor in the inter-tube van der Waals interactions. This, too, suggests that equally as reactive chloro-polymers might make equally as good

host materials. As an initial investigation, Poly vinyl chloride was used as a host and blended with MWNTs in an analogous fashion to the composites above. **Figure 7** shows the optical scattering from PVC-nanotube composites for 1%wt. loading and 0% loading. Surprisingly, these host materials show very little Rayleigh scattering. This, again, supports the general idea that the halocarbon nature of the host polymer can be used to disperse the nanotubes using low-shear blending methods.

It has been demonstrated in these examples that a new class of fluorocarbon matrix composites may be employed based on carbon nanotubes dispersed in fluoropolymer hosts. Clearly, other halo-polymers also could be used, with varying results depending upon the particular polymer selected, and the manufacturing and processing conditions. Different applications may use other types of halo-polymers, still within the scope of this invention.

Optical scatter and microscopy data suggests that dispersion can be directly controlled by adjusting the fluorine content of the polymer. Further, the role of the fluorine is mitigation of tube-tube interactions to allow for low-shear blending. These composites provide opportunities in the creation of new optically transparent, for example, and potentially electrically conductive films and the potential for new nonlinear optical materials.

In another application of the invention, the nanocomposite is employed as the sensing probe in atomic force and near field optical microscopes. The probe may employ a frontal face having a nanotube protruding therefrom as the sensing element. As an example, a carbon nanotube composite of the invention has the potential to dramatically improve spatial resolution of these scanning probe microscopes.

Figure 8a shows a drawn PFCB fiber containing carbon nanotubes. **Figure 8b** provides a micrograph of a near field optical probe using a frontal surface. In **figure 8b**, a near field optical probe 9 shows dispersed nanotubes 10. For example, the nanotube 10 shown may in some applications be approximately 0.4 µm from tip to

tip. Furthermore, a fiber frontal surface **11** is shown which corresponds to the ending point for one tip of the nanotube **10**. The field of view **12** (of the probe **9**) is shown beyond the fiber frontal surface **11**. The field of view **12** is the area under examination by

5   probe **9**.

As provided below, the compositions of the invention exhibit adequate thermal and electrical conductivity for these applications while maintaining mechanical flexibility, toughness, and, potentially, optical clarity. This is realized through the unique level of dispersion

10   for very low loadings (< 0.1 to 5 weight %) of high conductivity nanotubes in a halopolymer host.

PFCB chemistry is generally well suited for carbon nanotube composite fabrication. Carbon nanotubes can be easily and uniformly dispersed in trifluorovinyl ether (TFVE) monomers by gentle

15   sonication at ca. 70°C. Multi-walled and single walled nanotubes could be employed. Bulk polymerization of the mixtures results in optically clear nanocomposites at low loading levels. It is possible to fabricate nanocomposites containing isolated carbon nanotubes in fluoropolymers for both specialty coatings and nanoprobe

20   applications. Very low levels of well-dispersed nanotubes may be used in coatings which require multifunctional properties.

In the practice of the invention, it is possible to provide a halogen-containing polymer with carbon nanotubes, and to form a combined polymer matrix of dispersed carbon nanotubes within the

25   polymer matrix. There is no limit to the number of halogen-containing polymers that can be used in the practice of the invention. For example, polymers containing bromine, chlorine, iodine and fluorine are examples of halogens which can be incorporated into polymeric structures in the practice of the invention.

30

Example

Halo-Polymer Compositions With Clay Materials

Nanocomposite matrix compositions may be developed using halogen-containing monomers or polymers or co-polymers as described above in connection with the Examples (or other halogen-containing monomers or polymers as disclosed in this specification) as combined with various clay materials. For example, it is possible to provide in the matrix set forth in the examples above to include a clay product, such as a hydrated aluminum silicate (as one example).

Naturally occurring clays may be used, including but not limited to kaolinite, bentonite, mica, talc, silica nanoparticles, montmorillonite, attapulgite, illite, bentonite, halloysite, fullers earth, kaolin, and polyorganosilicate graft polymers.

There are numerous applications of the compositions of this invention, and the scope of this invention is not limited to any particular composition. It is understood by one of ordinary skill in the art that the present discussion is a description of exemplary embodiments only, and is not intended as limiting the broader aspects of the present invention, which broader aspects are embodied in the exemplary constructions. The invention is shown by example in the appended claims.

What is claimed is:

1. A composition prepared by combining

(a) nanomaterials, and

(b) a halogen-containing monomer.

2. The composition of claim 1 in which the nanomaterials comprise carbon-based nanotubes.

3. The composition of claim 2 in which the nanotubes are dispersed within a polymeric matrix, said polymeric matrix being formed by polymerization of said halogen-containing monomer.

4. The composition of claim 2 wherein the halogen-containing monomer comprises a monomer selected from the group consisting of: bromine, chlorine, fluorine, and iodine.

5. The composition of claim 2 in which the halogen of the halogen-containing monomer comprises fluorine, and further wherein said monomer is capable of polymerizing to form a fluoropolymer.

6. A polymeric composition prepared by combining

(a) nanomaterials, and

(b) a halogen-containing polymer.

7. The composition of claim 6 in which the nanomaterials consist essentially of carbon-based nanotubes.

8. The composition of claim 7 in which the nanotubes are spatially and orientationally randomly dispersed.

9. The composition of claim 7 in which the nanotubes are non-randomly dispersed.

10. The composition of claim 7 in which the halogen-containing polymer comprises a fluoropolymer.

11. The composition of claim 10 wherein the fluoropolymer comprises a trifluorovinylether.

12. The composition of claim 10 wherein the fluoropolymer comprises perfluorocyclobutane.

13. The composition of claim 6 in which the halogen-containing

polymer comprises a chloropolymer.

14. The composition of claim 13 wherein the chloropolymer comprises a vinyl chloride.

15. The composition of claim 14 in which the chloropolymer comprises poly(vinylidene-dichloride).

16. The composition of claim 13 in which the chloropolymer comprises chlorotrifluoroethylene.

17. The composition of claim 1 in which the nanomaterials are homogenously dispersed.

18. The composition of claim 7 in which the composition exhibits a thermal conductivity greater than 1.25 W/mK at a nanomaterial loading level from about 0.01 to about 10 weight %.

19. The composition of claim 7 in which the composition exhibits a volume resistivity of less than 10^{10} ohm cm at a nanomaterial loading level from about 0.01 to about 10 weight %.

20. The composition of claim 2 in which the composition exhibits an optical transmission of greater than 80 % at a nanomaterial loading levels from about 0.01 to about 80 weight %.

21. The composition of claim 7 in which the composition exhibits an optical transmission of greater than 50 % at a nanomaterial loading levels from about 0.01 to about 5 weight %.

22. The composition of claim 7 in which the composition exhibits an optical transmission of greater than 50 %.

23. A composition prepared by combining

(a) a halogen-containing monomer, and

(b) a clay material, said clay material comprising nanomaterials.

24. The composition of claim 23 in which the clay material is selected from the group of clay materials consisting of: bentonite, kaolinite, montmorillonite, attapulgite, illite, halloysite, fullers earth, kaolin, mica, talc, silica nanoparticles and polyorganosilicate graft polymers.

25. The composition of claim 24 in which the clay material comprises bentonite.

26. The composition of claim 24 in which the clay material comprises kaolinite.

27. The composition of claim 24 in which the clay material comprises silica nanoparticles.

28. A polymeric composition prepared by combining

(a) a halogen-containing polymer, and

(b) a clay material, said clay material comprising nanomaterials.

29. A composition comprising:

(a) carbon-based nanotubes, and

(b) a chloride-containing polymer.

30. The composition of claim 29 in which the polymer comprises poly(vinylchloride).

31. The composition of claim 29 in which the polymer comprises poly(vinylidene-dichloride).

32. The composition of claim 29 in which the polymer comprises a vinyl chloride.

33. A composition prepared by combining

(a) carbon-based nanotubes; and

(b) a halogen-containing polymer, wherein the halogen-containing polymer includes at least one halogen selected from the group consisting of fluorine, chlorine, bromine, and iodine;

(c) thereby forming a combined polymer matrix having dispersed carbon nanotubes within the polymer matrix.

34. The composition of claim 33 in which the halogen-containing polymer comprises a fluoropolymer.

35. The composition of claim 33 in which the halogen-containing polymer is copolymerized using a monomer of triflurovinyl ether (TFVE).

36. The composition of claim 34 in which the fluoropolymer comprises a perfluorocyclobutane (PFCB) aromatic ether polymer.

37. A composition formed by combining:

(a) carbon nanotubes, and

(b) a copolymer comprising a poly-aryl ether with perfluoroocyclobutyl (PFCB) linkages.

38. The composition of claim 37 in which the copolymer is prepared from a trifluorovinyl aromatic ether.

39. A probe for microscopy, comprising:

a fiber with a frontal surface comprised of a polymeric matrix having dispersed carbon nanotubes within the polymeric matrix.

40. A composition prepared by combining

(a) carbon-based nanotubes,

(b) a halogen-containing monomer, and

(c) a naturally occurring material selected from the group of materials consisting of: Group IIII elements and Group V dopants.

41. The composition of claim 40 in which the naturally occurring material is combined with a halogen-containing monomer.

42. The composition of claim 40 in which the naturally occurring material is combined with a halogen-containing polymer.

43. The composition of claim 40 in which the naturally occurring material is combined with a nanomaterials.

FIGURE 1a
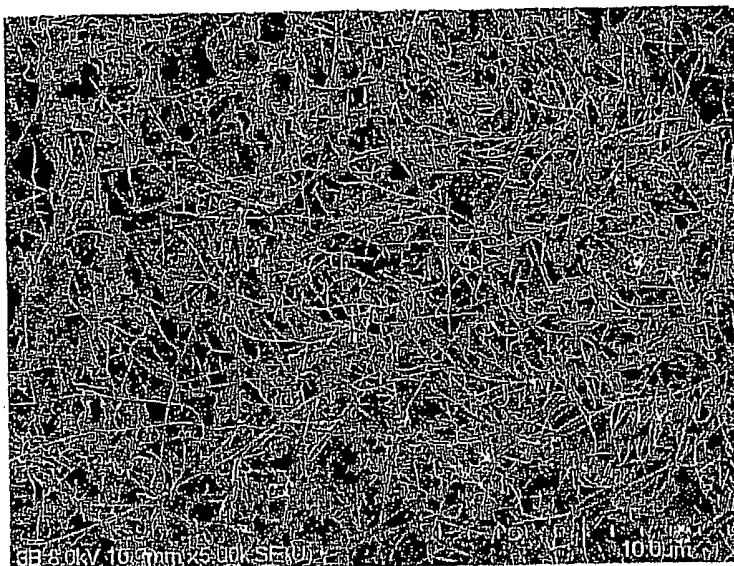
FIGURE 1b

FIGURE 1c

1.0kV 5.8mm x9.01k SE(U) 2/13/01 15:18   5.00um
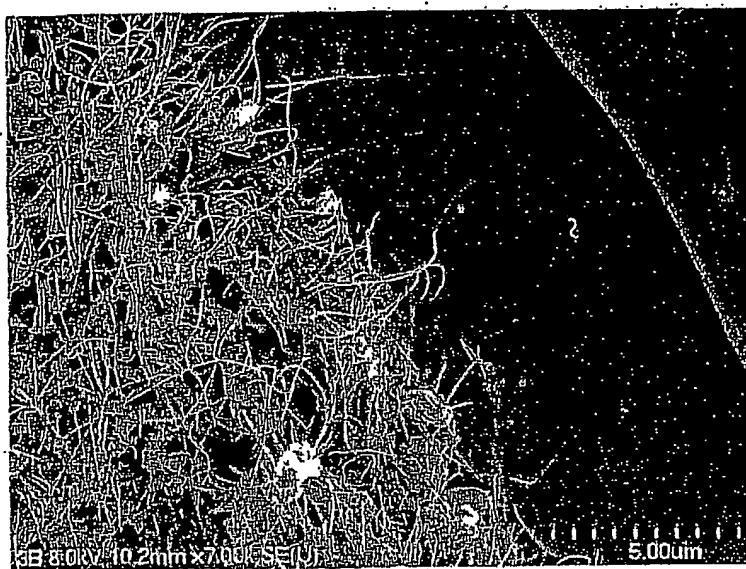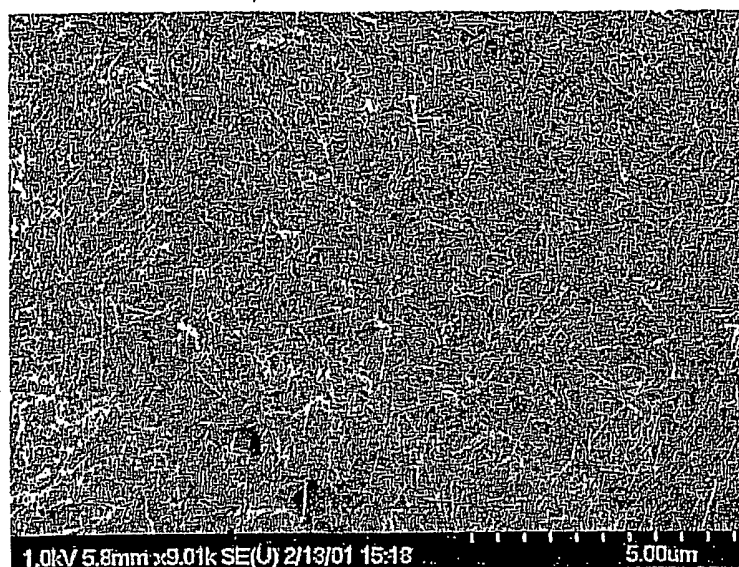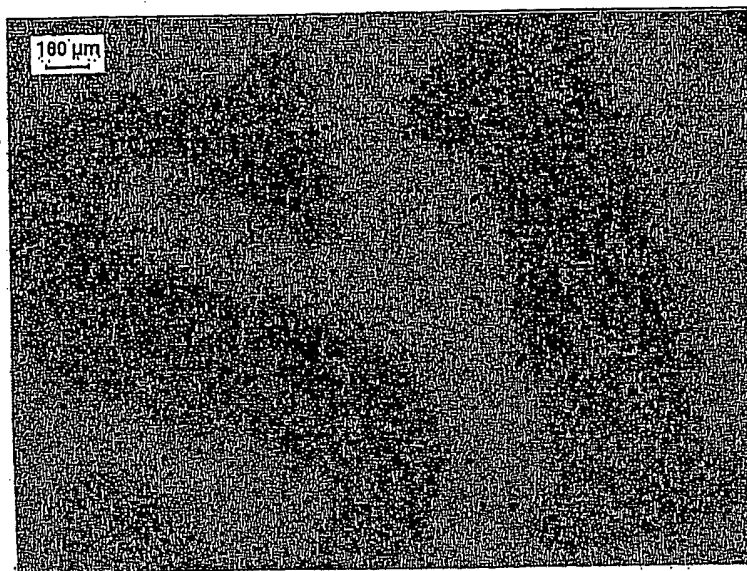
FIGURE 1d
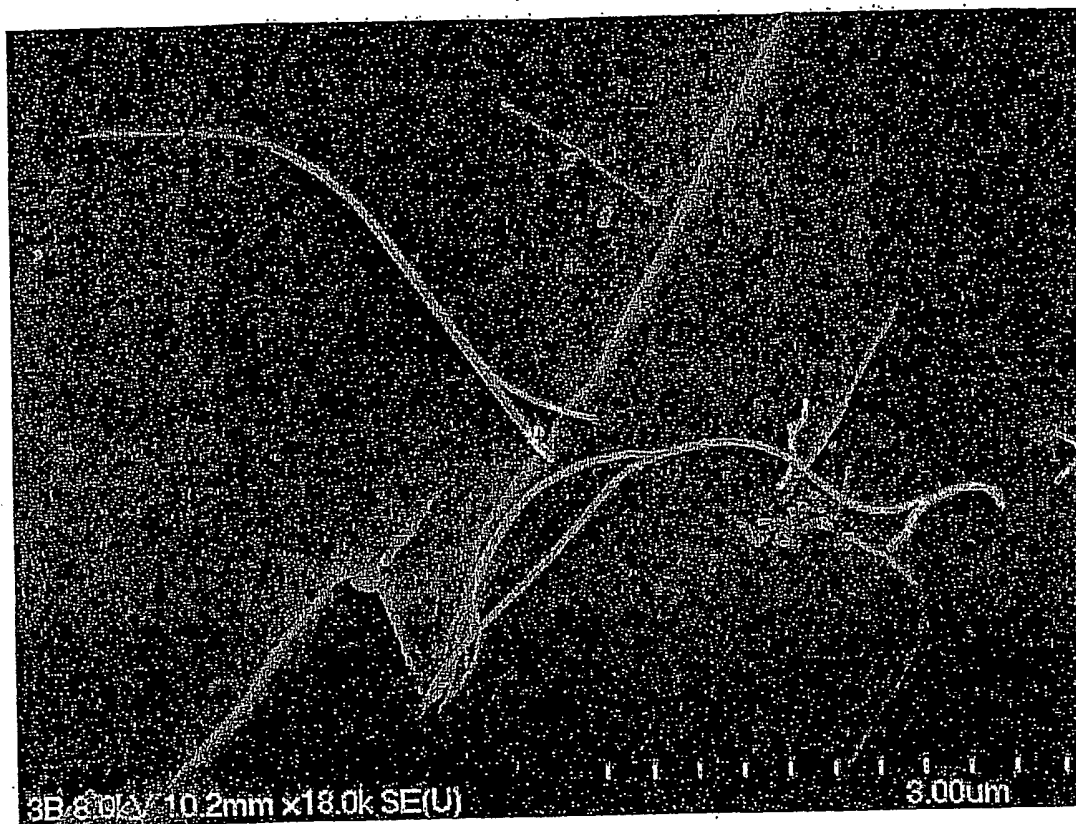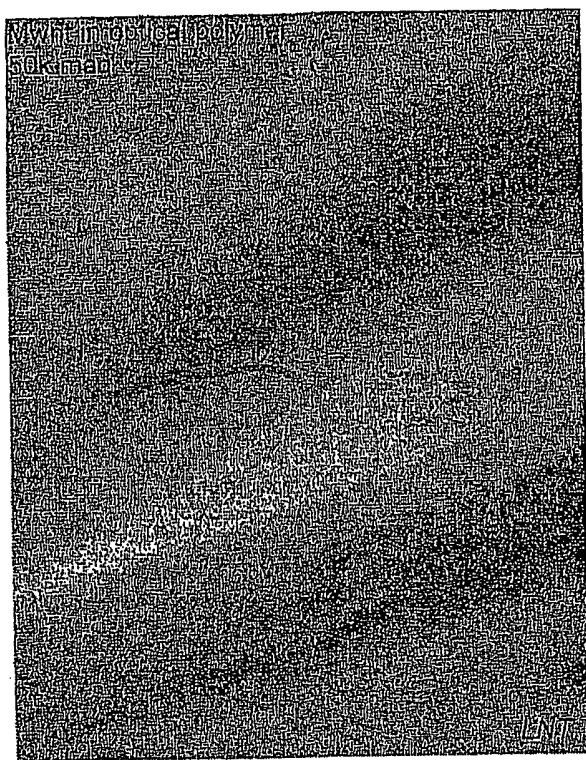
FIGURE 1e

FIGURE 1f

FIGURE 2a

FIGURE 2b
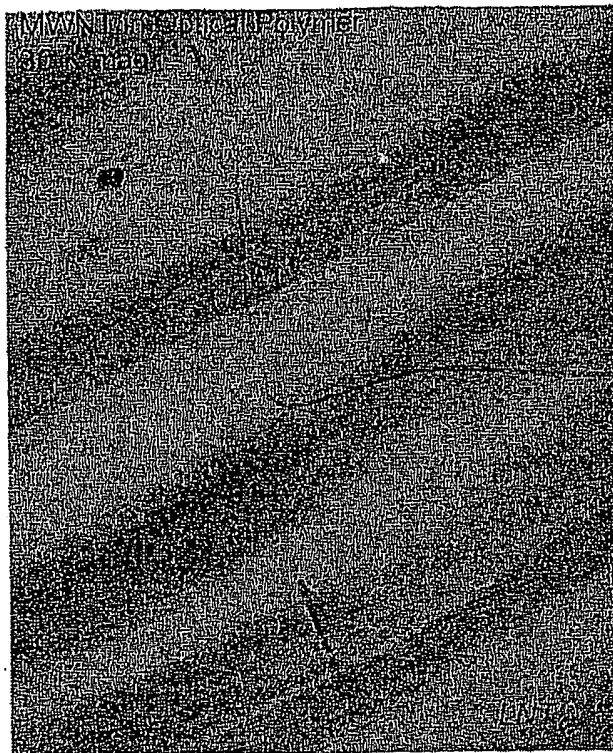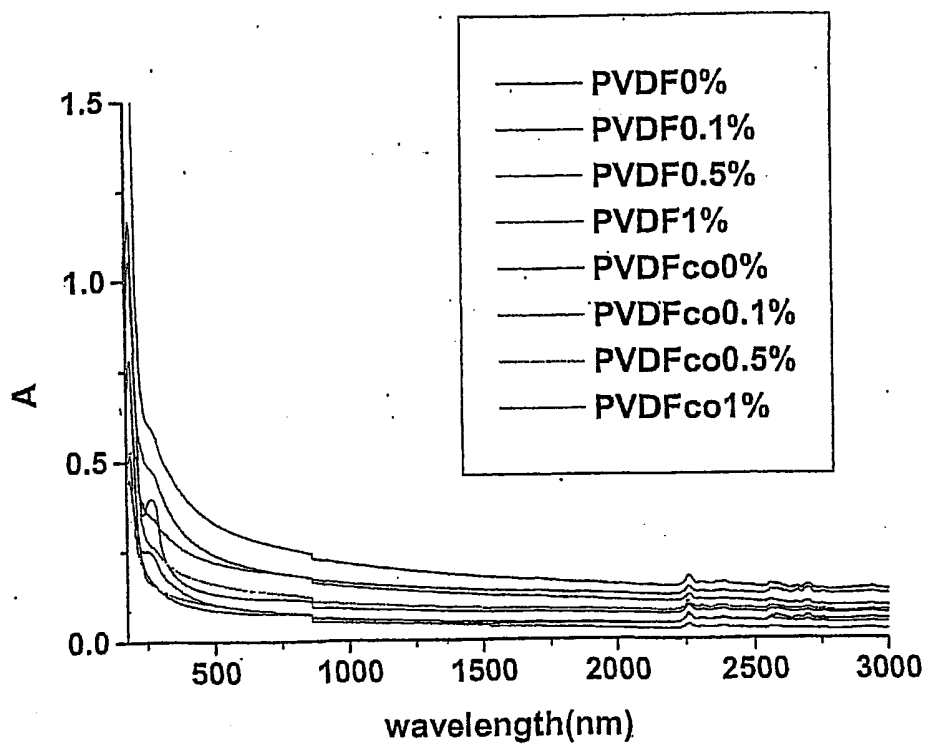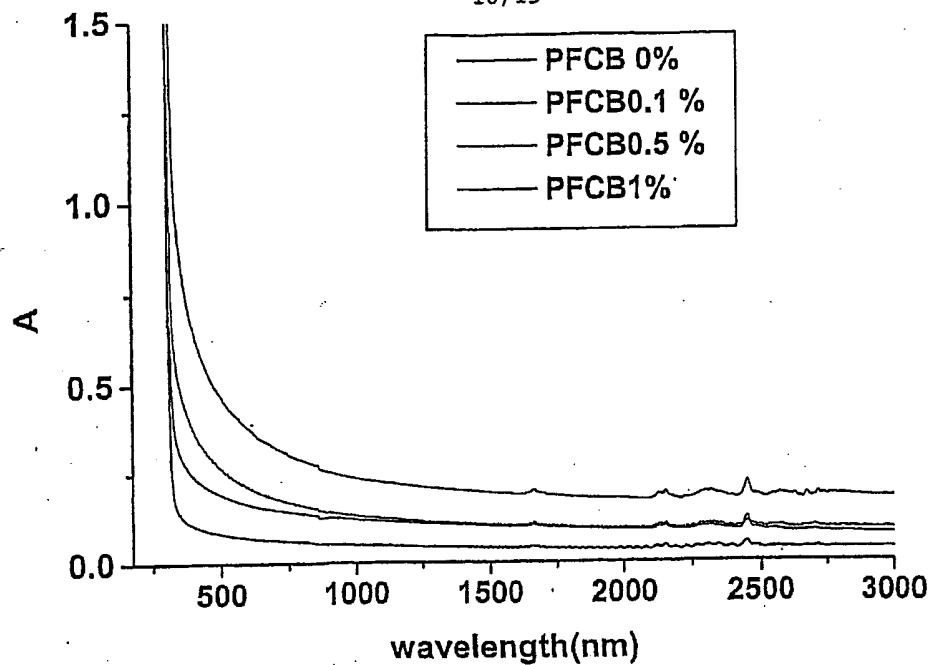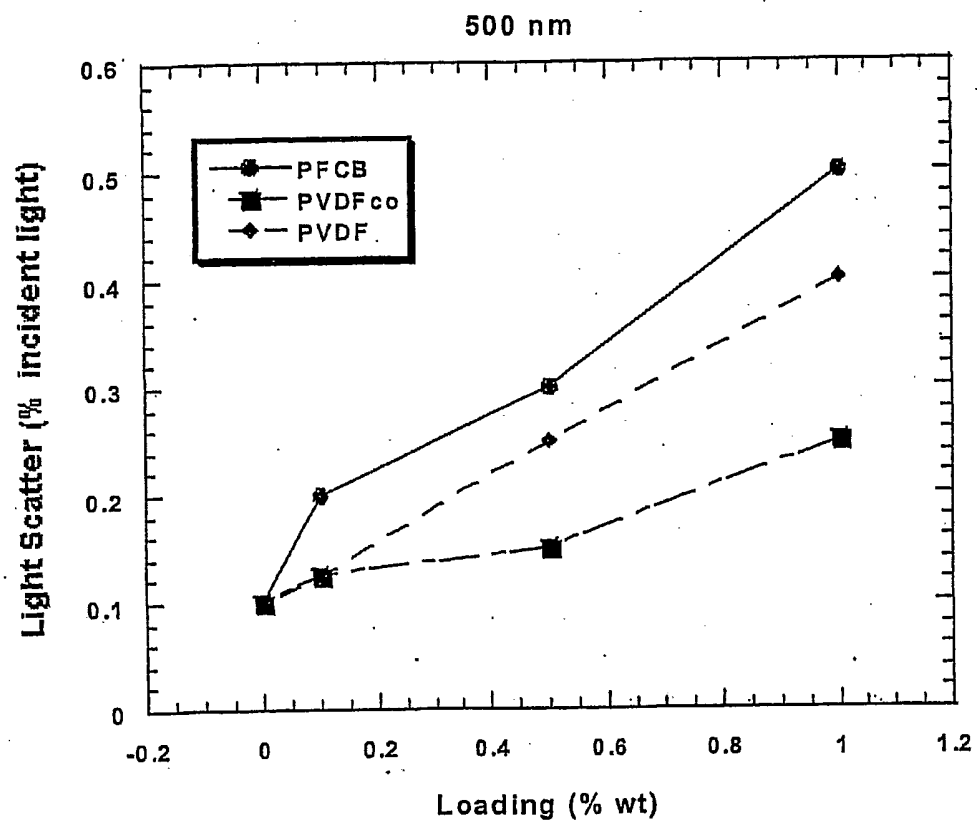
FIGURE 2c
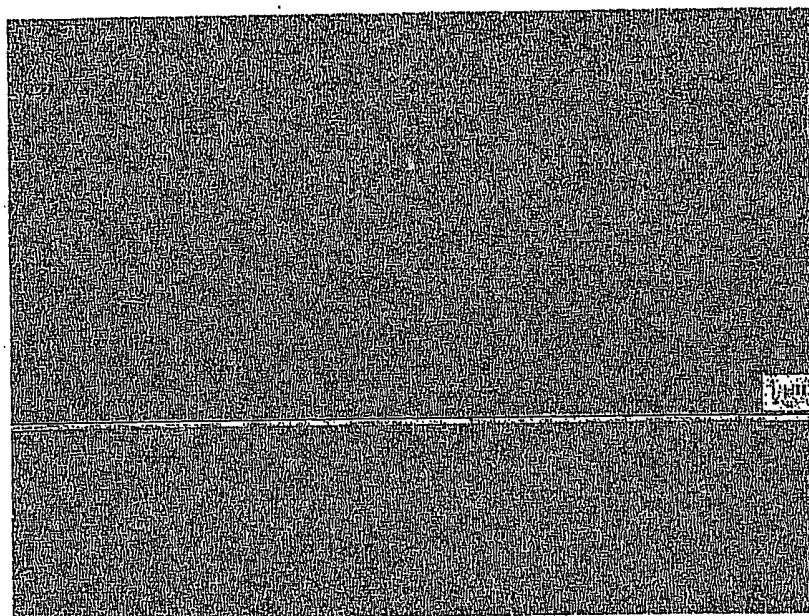
FIGURE 3

FIGURE 4

FIGURE 5

	$\gamma_{polymer}$ (dynes/cm)	Fluorine (atom%)	Dispersion (est.)
PMMA	37	0%	poor
PFCB	37.8	18.5%	good
PFCB co	37.8	25%	good
PVDF	25	33%	excel.
PVDF co	....	53%	best

FIGURE 6
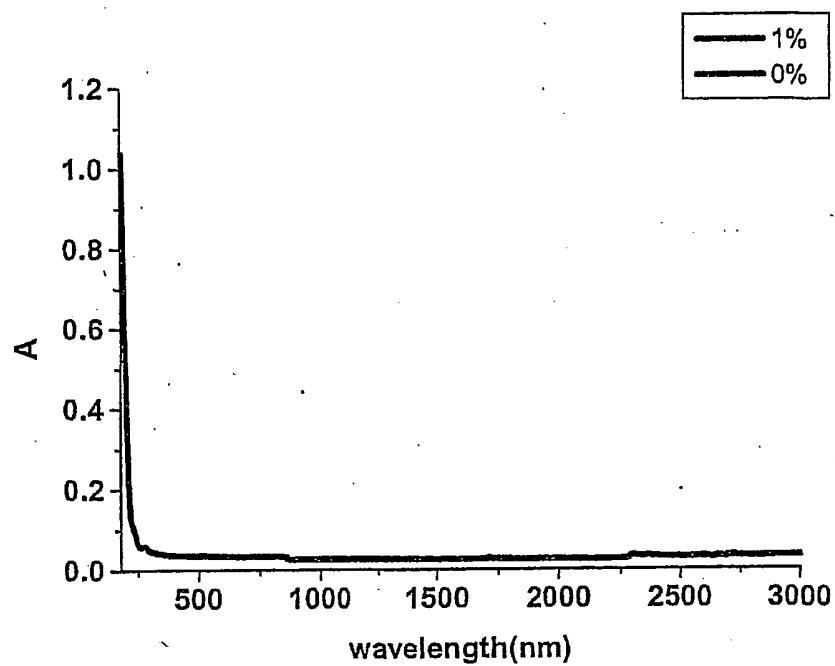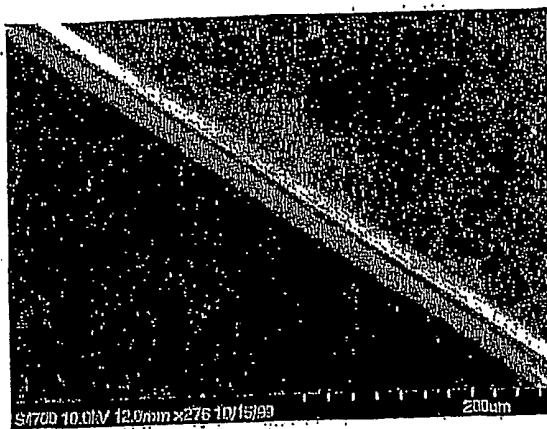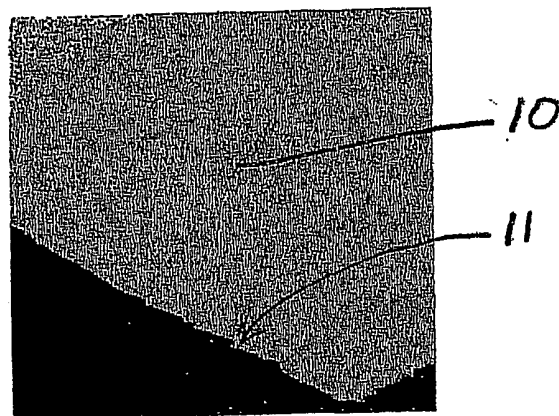
FIGURE 7

FIGURE 8a

FIGURE 8b

(51) International Patent Classification⁷: C08K 3/04, 3/34

(21) International Application Number: PCT/US02/08913

(22) International Filing Date: 22 March 2002 (22.03.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/278,015   22 March 2001 (22.03.2001)   US
10/103,562   21 March 2002 (21.03.2002)   US

(71) Applicant: CLEMSON UNIVERSITY [US/US]; 300 Brackett Hall, Clemson, SC 29634-5701 (US).

(72) Inventors: CARROLL, David; 219 Luna Lane, Central, SC 29630 (US). BALLATO, John; 811 Issaqueena Trail, Central, SC 29630 (US). FOULGER, Stephen; 301 Monaco Circle, Clemson, SC 29631 (US). CZERW, Richard; 102 Sedgefield Drive, Clemson, SC 29631 (US). SMITH, Dennis; 3010 North Bayshore Drive, Seneca, SC 29672 (US). SHAH, Hiren; 146 Folger Street, Clemson, SC 29631 (US). WAGENER, Earl; 216 Strawberry Lane, Clemson, SC 29631 (US).

(74) Agent: DORITY & MANNING, P.A.; P.O. Box 1449, Greenville, SC 29602 (US).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— with international search report

(88) Date of publication of the international search report:
19 December 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: HALO-POLYMER NANOCOMPOSITE COMPOSITIONS, METHODS, AND PRODUCTS EMPLOYING SUCH COMPOSITIONS

3B 2.0kV 9.2mm x35 SE(U)   1.00mm

(57) Abstract: The disclosure provides compositions prepared by combining nanomaterials with a halide-containing polymer, thereby forming a combined polymer matrix having dispersed nanomaterials within the matrix. The nanomaterials may be carbon-based nanotubes, in some applications. A halide-containing monomer is combined with nanotubes, and then polymerized in some compositions. In other applications, a holide-containing polymer is solution processed with nanotubes to form useful compositions in the invention. Also disclosed are probes for near field detection of radiation.

WO 02/076903 A3

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :C08K 3/04, 3/34

US CL : 524/445, 447, 449, 451, 492, 493, 495, 496

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/445, 447, 449, 451, 492, 493, 495, 496

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

West

search terms: nanocomposite, nanotube, kaolin, bentonite, mica, talc, silica

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,E	US 6,414,070 A (KAUSCH et al) 02 July 2002, abstract and claims.	1-43
Y,E	US 6,407,155 A (QUIN et al) 18 June 2002, abstract and claims.	1-43
Y,E	US 6,395,386 A (BAGRODIA et al) 28 May 2002, abstract and claims.	1-43
Y	US 6,126,734 A (BEALL et al) 03 October 2000, abstract and claims.	1-43
Y	US 6,124,365 A (LAN et al) 26 September 2000, abstract and claims.	1-43

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 SEPTEMBER 2002	03 OCT 2002

Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer EDWARD CAIN DEBORAH THOMAS PARALEGAL SPECIALIST
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet) (July 1998)*

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/08913

Box I   Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II   Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite paym· of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search rep covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search repo restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest   ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet(1)) (July 1998)✶